Full Length Article

Gasification kinetics of lignite char in a fluidized bed of reactive oxygen carrier particles

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A B S T R A C T

The conversion of lignite under Chemical Looping Combustion conditions differs sharply from air-fired combustion as high volumetric gas concentrations of CO_2 and steam prevail in the reactor and the oxygen for the fuel conversion is provided by a solid oxygen carrier. In this work a lab scale fluidized bed reactor (ID = 53 mm) was used to measure the conversion behavior of German Rhenish lignite under Chemical Looping Combustion conditions. The carrier used was 14 wt-% copper oxide on γ-alumina. Special focus was laid on the particle size of the char during gasification, hence 3–6 different size fractions, in the range of 150–1500 μm were converted during each test series, respectively. The gasification experiments showed that gasification of lignite in a fluidized bed of inert sand particles is slightly faster for steam compared to CO_2 gasification. In the inert sand bed, chemical reaction limitation of the kinetics could be seen for all lignite size fractions below 850 μm diameter. Gasification rates were in the range of literature findings for fluidized bed gasification in inert sand beds. The inhibition effects of both CO and H_2 were reproduced by applying CO and H_2 as fluidization gases during gasification. Gasification experiments in a fluidized bed of a completely oxidized oxygen carrier showed for both CO_2 and steam gasification an enhancement of the char conversion, even more for smaller particle sizes of the lignite. Simultaneous gasification with CO_2 and steam showed only slight increases in the measured gasification rates compared to steam only gasification. The Shrinking Core Model was generally able to describe the experiments. A resistance approach was used to describe the strong mass transfer limitations seen in the reactive bed for larger char particles particularly at higher temperatures. Kinetic parameters were extracted for the simultaneous steam and CO_2 gasification under in-situ Gasification Chemical Looping Combustion conditions.

1. Introduction

Lignite remains a major fossil fuel in electricity generation around the globe. Unfortunately, the fuel is connected with high carbon dioxide emissions per electricity produced. It was shown in several studies, e.g. Thomaszewicz et al. [1] that after drying and devolatilization lignite char is more reactive during gasification than the coals with higher content of fixed carbon. Due to the high carbon dioxide emissions on the one hand and the high reactivity on the other hand, lignite is well suited for carbon capture and sequestration technologies.

Chemical Looping Combustion (CLC) is such a technology in which fuels are indirectly oxidized by an oxygen carrier (OC). The oxygen transport is arranged by the reducing and oxidizing of a metal oxide, often shortened as M_xO_y. The OC is circulated between an air reactor (AR), where gaseous oxygen is bound to the carrier and a fuel reactor, where the solid OC reacts with the gasified or gaseous fuel in the absence of ambient air. One major conversion route in CLC is the so called

in-situ Gasification-CLC (iG-CLC), which is depicted in Fig. 1. There, the solid fuel is directly fed into the fuel reactor (FR), where it dries, devolatilization takes place and later the char is gasified. The product gases from the gasification CO and H_2 can react further with the OC to the main flue gases steam and CO_2. Steam is being condensed and, with it, removed easily from the flue gas. Hence, a pure stream of CO_2 is generated in the CLC process.
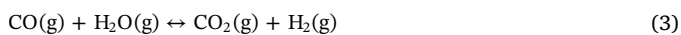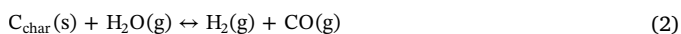
Lignite gasification in the fluidized bed even dates back to 1926, when a fluidized bed reactor was applied to generate syngas [2]. In the last decades, the reaction kinetics of char gasification in inert bed fluidized bed reactors was widely investigated and reference literature, e.g. Johnson et al. [3], describe the mechanisms of CO_2-char gasification, steam char gasification and pressurized gasification. The basic gasification reaction Eqs. (1) and (2) describe the conversion of the main reactants in this heterogeneous gas-solid reaction. The complexity of steam and CO_2 gasification is increased by the homogeneous water-gas-shift (WGS) reaction, Eq. (3), because the gasification agents H_2O

Nomenclature

Abbreviations

CLC	Chemical Looping Combustion
CLOU	Chemical Looping with Oxygen Uncoupling
iG-CLC	in-situ Gasification Chemical Looping Combustion
FR	Fuel reactor
AR	Air reactor
OC	Oxygen carrier
TGA	Thermo-gravimetric analysis

Symbols

X_s	Char conversion [–]

d_S	Sauter mean diameter [m]
$F_{i,j}$	Volumetric flow of component i in flow j [m^3/s]
$R_g(X_s)$	Rate of gasification [1/s]
$R_{g,inst}(X_s)$	Instantaneous rate of gasification [1/s]
$k_{model}(T, x_i)$	Kinetic parameter for a set of operation conditions [1/s]
k_g	Kinetic parameter for the diffusion
Ψ	Pore opening factor in Eq. (17) [–]
k_0	Pre-exponential factor in Eq. (19) [1/s]
x_i	Molar fraction of component i [–]
n	Reaction order [–]
u_R	Superficial gas velocity at the distributor level, not considering volumetric flow changes cause by chemical reactions [m/s]

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and CO_2 are converted into each other depending on the equilibrium of the reaction.

$$C_{char}(s) + CO_2(g) \leftrightarrow 2CO(g) \tag{1}$$

$$C_{char}(s) + H_2O(g) \leftrightarrow H_2(g) + CO(g) \tag{2}$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \tag{3}$$

According to Matsui et al. [4–6], a Langmuir Hinshelwood type kinetics can be applied for both steam- and CO_2-gasification of coal char, which are defined in Eq. (4) for steam and (5) for CO_2.

$$\frac{dX_s}{dt} = \frac{k_1[H_2O]}{1 + k_2[H_2O] + k_3[H_2] + k_4[CO]} f(X_s) \tag{4}$$

$$\frac{dX_s}{dt} = \frac{k_1[CO_2]}{1 + k_2[CO_2] + k_3[CO]} f(X_s) \tag{5}$$

One can see that the solids conversion per unit time $\frac{dX_s}{dt}$ is on the one hand depending on the kinetic constants and the kinetics of each participating gas species and on the other hand depending on the state of the char conversion X_s. This latter phenomenon is expressed by the function $f(X_s)$. The kinetic parameters k_1 to k_4 describe the effects of the participating gases in their respective concentrations.

In the FR of an iG-CLC plant, the solid fuel is at first converted to syngas, which then can react further with the OC. This means that in contrast to the gasification in an inert sand bed, the main gasification products CO and H_2 are constantly removed from the gas stream in the

reactor. The effect of CO and H_2 on the gasification rates is already included in the mechanisms above as they appear in the denominator of Eqs. (4) and (5). The removal of those inhibiting gases could lead to a major enhancement of the gasification rate and the process performance of CLC. In a fluidized bed reactor, the OC conversion products CO_2 and H_2O will also contact again with unreacted coal char, which will also enhance gasification. The reaction mechanism is depicted in Fig. 2, as described previously by Adanez et al. [7] or Lyngfelt et al. [8], but extended here for the reaction of the oxygen carrier conversion products with the coal char.

The heterogeneous reaction between the fuel gases CH_4, CO and H_2 with the OC can be investigated via thermogravimetric analyzing (TGA) methods. However, the kinetics of the char conversion in a reactive fluidized bed cannot sufficiently be determined in a TGA. This is due to gas-solid mixing and fluid mechanics inside a fluidized bed, which are impossible to achieve in a TGA pan. Hence the interactions of the two reactive solids and their implications should if possible be investigated in a fluidized bed reactor. The conversion kinetics of solid fuels is a major design criterion for iG-CLC as the slip of unconverted char from the FR to the AR has to be avoided. To investigate the effects of reactive bed material, like ash or the OC, on the conversion, fluidized beds have to be used. Unfortunately, with the application of fluidized beds, problems arise in the evaluation of the experimental data. First of all, the effects of the char conversion cannot be directly and instantaneously measured as in a TGA, but have to be derived from mass balances established via gas concentration measurements. Additionally, hydrodynamic phenomena, like bubbles in a bubbling fluidized bed, lead to a bypass of gas, which does not take part in the heterogeneous reactions.
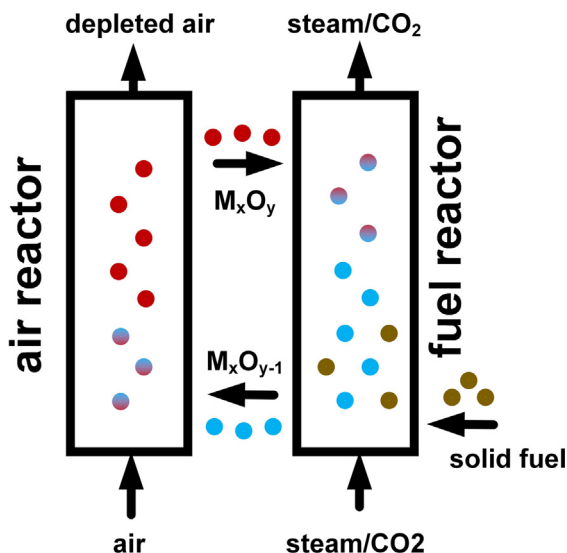

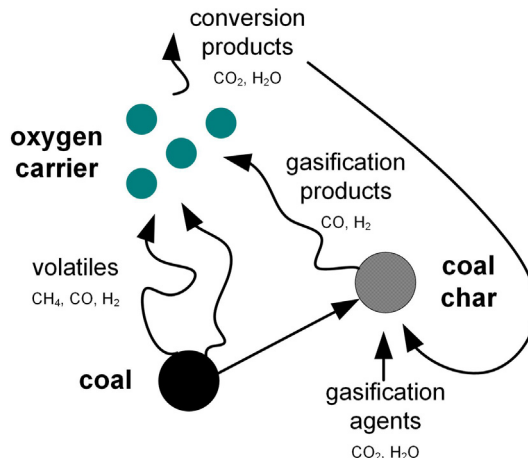**Fig. 1.** Process schematics of the iG-CLC process.

Fig. 2. . Coal conversion route for coal as solid fuel. From Adanez et al. [7], but extended for the effect of conversion products on gasification.